DIOXIN-LADEN RESIDUAL STREAMS FROM THERMAL AND METALLURGICAL PROCESSES: INVENTORY AND MANAGEMENT

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Introduction

On behalf of Aminabel, the Planning Division of the Flemish Administration for the Environment, Nature, Land & Water Management, an inventory was prepared of all dioxin-laden residual streams arising in Flanders in thermal and industrial plant & processes, more in particular in the following 7 major sectors of activity: 1) metallurgy; 2) cement, glass, and ceramic industry; 3) power plant; 4) oil refineries; 5) industrial boilers and domestic heating; 6) vinyl chloride manufacturing; and 7) waste incineration. It was expected to gather in this scope all major flows of dioxin containing residues in Flanders, with only three exceptions, namely those arising from (a) *cold sources*, (b) various *historical sinks* and (c) *import* of materials.

Other tasks included: studying *the trajectories* taken by the various residual streams, *evaluating the risk* associated with their disposal, indicating a *Best Available Technology* for their treatment, identify further *issues of concern*, and finally, suggest *measures for management*, whether based on dedicated new legislation, further specification or completion of existing rules, or more active implementation of monitoring, inspection, etc. within the current legal framework.

Methods and Materials

The following working method was followed for dressing an inventory of all relevant dioxin streams (Mtonnes/year), considering their eventual fate, and the flow of dioxins (g I-TE/year) associated:

1. Industrial enterprise annually is held to notify a Public Authority (OVAM) of all waste arising (regular process waste and also incidentally). All such streams are classified by a specific code (AKO), and their amount, description, transporters, and destination are recorded.
2. For each individual enterprise belonging to a certain sector of industrial activity (retrievable by a NACE-Code) the notification data could be studied, checked, corrected where needed, and ultimately totalled per kind of waste, and this per sector of industrial activity. Attention was only paid to those streams originating from potentially dioxin generating processes.
3. Data on the unit load of dioxin streams were gathered either on the basis of prior knowledge, or by a thorough literature search. This data was combined with the flow rate of the various residual streams, leading to an inventory of the flow of dioxins (g I-TE/year) associated with these streams.
4. Examples of wastes studied include: filter dust, wastewater sludge, foundry sand, refractory, slag, metal, as well as incidental streams, e.g. arising from boiler or chimney cleaning, catalyst replacement, disposal of plastic construction materials.

Results and Discussion

Best Available Technology what is the Best Available Technology (BAT) to be used in case a dioxin-laden stream must be decontaminated? Such (process integrated) decontamination of residues has now become general for new MSWI-plants in Japan, but is still not customary in Europe. In a wide literature survey, encompassing a patent study, the Proceedings of Dioxin 2000 and Dioxin 2001, and a computer search of the data system of the University of Umeå, a large number of thermal, physicochemical, biochemical, and even mechanical methods were identified. Despite the merits of the various initiatives studied, it is fair to state that only thermal methods at present pertain to the State-of-the-Art, more in particular those using:

1. Low temperature treatment under inert or reducing conditions, such as the Hagenmaier trommel, or the Sumitomo activated carbon regeneration system.
2. Medium temperature treatment under oxidising conditions, and high temperature treatment under slagging conditions.

Moreover the thermal destruction of dioxins is expensive from a viewpoint of both investment and operating cost. Hence preference should be given to integrated methods of dioxin reduction, i.e. preventing or reducing formation by selecting appropriate technology and operating conditions. Inhibition can be used as a potent pathway in prevention, and so can a sudden quench of off-gases, reducing the temperature from a level around 450 – 500 °C to a mere 200 °C. Avoiding deposits in boilers, transfer lines, and hoppers can also be important in reducing generation of dioxins. These remarks apply mainly to incineration and to metallurgical processes, but may also be extended to cement manufacturing, chloride chemistry, etc.

Measures for Management

From recent reviews[1,2] it follows that the E.U. as yet has no policy for monitoring dioxin-laden residues and that the Guidelines available in other Countries centring on dioxin-contaminated soil present disparate values. Recently a comprehensive Japanese Law[3] was published, putting in perspective an integrated approach of reducing dioxins in the Environment, even though there is much more emphasis on Incineration than on other industrial activities. Limit values in several domains will be fixed with the respect of an ADI as a driving force. EPA[4] has proposed mandatory analysis of listed commercial products that may be dioxin contaminated and also Switzerland[5] showed attention for dioxin problems, even dressed a National Inventory[6] showing in- & outflows, the latter mainly incineration and metallurgical residues, as well as the waters from the Rivers Rhine and Rhône!

In principle, the present legal context in Flanders already offers a number of possibilities for controlling dioxin-contaminated residues, specifying in detail procedures for Licensing and for Inspection of duly licensed industrial facilities. Moreover, the compulsory annual Notification of all waste streams, as well as the obligation of producing an annual Environmental Report detailing all emissions and waste streams from all activities in principle offers opportunities for monitoring and evaluating the status of affairs regarding all pollutants. In practice, however, there is as yet no general legal obligation of performing or publishing dioxin analyses, and discreetly some enterprise prefer not to mention this somewhat terrible sounding pollutant. For this reason it should be considered how and by which means to activate further measures to be taken by enterprise, e.g. of dioxin identification, prevention, and monitoring in all external streams, especially those being put into trade. An ideal situation can be summarised as:

1. Enterprise is aware of all its *incoming* dioxin streams. Since the input flows are known, upward pressures can be exerted to reduce such loads on the raw materials taken in.
2. Operators are familiar with *in-plant de novo formation,* and the factors that control dioxin generation. They also established the Destruction & Removal Efficiency (DRE) of their processes and have developed a Long-Term Strategy for reduction of dioxin outputs.
3. Input and output flows are monitored with the necessary frequency, so that any hazards can be evaluated and minimized, and balances established.

Possible measures to be taken can be summarized as:

- Dioxin monitoring;
- Measures of identification;
- Measures of prevention;
- Measures relative to commercial commodities;
- Measures required for materials selected for useful application

Much support was received from all branches of industry concerned, as well as from the various environmental authorities (OVAM, VMM), including the Inspectorate Division of Aminal. Yet a number of intrinsic difficulties could be identified:

1. Obligatory notification generally creates no problem in major industrial corporations. On the other hand, it proved problematic to obtain correct, convincing and complete data from small enterprise (< 50 people) and the same holds for ‘trivial’ residual streams, such as wood ash.

2. In some cases corrections had to be made, because some flows are not always classified the same way, or further information was to be taken from relevant enterprise. Obviously, this necessitated a considerable investment in time, and caused an increase in the duration and efforts to be made.

3. A large number of metallurgical streams, and often of filter dust heavily charged with dioxins, was not retrievable by studying waste notification because these streams were either recycled internally, or sold externally for the value of metals contained, the processing cost deducted. Similarly, it proved impossible to dress a representative inventory of dross, skimming, and other metal oxides, since these are recovered and sold as commercial products.

4. Some sectors are poorly documented. So the available data was negligible, or even non-existing for oil refineries, brick making, glass manufacturing. Though these sectors are not considered to be large sources of dioxins, it was not possible to assign accurate values for these sectors and further efforts are warranted.

5. Another problem was assigning accurate values to the dioxin-laden streams. This problem was double: high values for the dioxin load can often strongly vary from plant to plant, operation to operation, or day to day, so that the result may eventually depend on a few high flying values. Conversely, low values as for slag or refractory are almost non-documented, but must often be multiplied by a huge mass stream, possibly of as much as 0.1 to 1 Mtonnes/year.

6. A last problem was that of the actual value of some of the data obtained, since on the one hand there were a lot of changes in some sectors during the last few years, on the other the notification in some sectors was not respected, so that the results were not representative.

Proposal for a management system can be realized by the following stepwise approach:

1. *Identification* of all potentially dioxin laden streams originating in thermal or metallurgical processes (extension to chlorine based processes can be considered),

2. *Monitoring their eventual fate* (landfill, recycling, or other use), in case a certain limit threshold value is exceeded,

3. *Defining a threshold value* above which the dioxin-laden stream qualifies as “hazardous” as well as a value, below which the dioxin-laden stream becomes assimilated to background and hence of no further concern. These values can best be fixed on a basis of international consensus, and confronted with analytical practicalities, such as detection limits and difference in fingerprints and I-TE values. The latter may mask high concentrations, if in OCDD/F!

The proposed system is to be based upon the following steps:

1. *Implementing a comprehensive identification system* of all streams of thermal or metallurgical origin and that are a potential dioxin carrier. This is simply realized, by applying the criteria cited in TRGS 557[7],

2. *Defining a strategy of sampling & analysis*, and

3. *Proposing a subdivision in white flows* (no more dioxins than a *background level* to be selected), *black flows* (*notable dioxin carrier*, to be monitored constantly), and *grey flows* (*feeble dioxin carrier*, to be monitored periodically).

The Aminal Study considered numerous processes in great detail and discovered hitherto not identified sources of dioxins, generally however without much consequence. At present the danger exists that part of dioxin-laden streams are not identified as such, for several streams figure on the Green List that can normally be expected dioxin-laden. Moreover, trivial flows from cleaning may be lost out-of-sight, even though their charge may be considerable. If dioxin-laden streams are clearly marked, they can be considered 'hazardous' chemicals or residues, paving the way to their treatment with known legal means, i.e. the usual Rules regulating labelling, packing, transport & storage. Handling on the workfloor can be inspired by the specific German Code TRGS 557[7].

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